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OFFICE OF  
PREVENTION, PESTICIDES AND  
TOXIC SUBSTANCES

OPP OFFICIAL RECORD  
HEALTH EFFECTS DIVISION  
SCIENTIFIC DATA REVIEWS  
EPA SERIES 361

February 13, 2001

MEMORANDUM

Subject: Reregistration of **Mancozeb and Metiram**: Apple Processing and Reduction of Residue Studies; Chemical Nos. 14504 and 14601; DP Barcodes D229954 ; MRID Nos.: 44064001 and 44101101

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To: Anne Overstreet  
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The EBDC/ETU Task Force has submitted processing studies to support the reregistration of mancozeb and metiram on apples. These studies have been reviewed by Dynamac Corporation under supervision of HED, and the review has been revised to reflect Division policies.

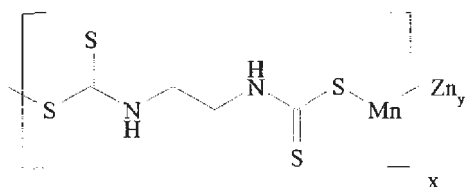
No additional apple processing studies are required to support the tolerance in/on apples. No processed commodity tolerances are needed for mancozeb, but a tolerance for residues of metiram and ETU in wet apple pomace must be proposed. Reduction of residue data indicate metiram residues in/on fresh apples during typical packing and processing procedures. The data for mancozeb were inadequate, so no conclusions can be made regarding reduction of residues

for apple packing and processing.

cc: COlinger, Reg. Std. File,  
7509C:RRB1:CLOlinger:clo:CM#2:Rm 722J:305-5406:1/17/01  
RDI: FFort: 02/8/01; WPhang: 02/12/01

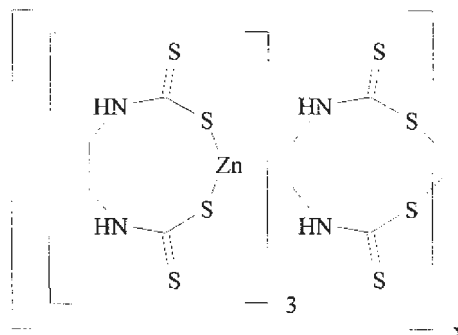


## MANCOZEB



PC Code No. 014504

## METIRAM



PC Code No. 14601

(DP Barcode D229954)

### REGISTRANT'S RESPONSE TO RESIDUE CHEMISTRY DATA REQUIREMENTS

#### BACKGROUND

In response to the Mancozeb Reregistration Standard Update, dated 8/11/92, and the Metiram Reregistration Standard Update, dated 8/11/92, the EBDC/ETU Task Force [with members consisting of Elf Atochem North America, Inc., BASF Corporation, E.I. du Pont de Nemours and Co., Inc., and Rohm and Haas Company] has submitted data pertaining to the magnitude of mancozeb, metiram, and ETU residues in apple processed commodities (1996; MRID 44101101) and reduction of residue data for apples (1996; MRID 44064001). The submitted studies are evaluated herein for their adequacy in fulfilling residue chemistry data requirements for the reregistration of mancozeb and metiram. The Conclusions and Recommendations stated in this document pertain only to the magnitude of mancozeb, metiram, and ETU residues in apple processed commodities. Other data requirements stated in the Mancozeb or Metiram Updates are not addressed herein.

We note that all mancozeb products registered by DuPont were transferred to Griffin Corporation on 4/8/98.

The qualitative nature of mancozeb residues in plants and livestock is adequately understood (R. Perfetti, 10/4/93, Barcode No.: D193431). Mancozeb and ethylenethiourea (ETU) are the residues of concern. The qualitative nature of metiram residues in plants and livestock is adequately understood. Metiram and ETU are the residues of concern.

Tolerances for residues of mancozeb in/on plant and animal commodities are currently expressed in terms of residues of a fungicide which is a coordination product of zinc ion and maneb (manganous ethylene bisdithiocarbamate) containing 20 percent manganese, 2.5 percent zinc,

and 77.5 percent ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate) [40 CFR §180.176 and §180.319]. The Agency has recommended that the tolerance expression for mancozeb be revised to include residues of ETU.

Tolerances for residues of metiram in/on raw agricultural commodities are currently expressed in terms of residues of a fungicide which is a mixture of 5.2 parts by weight of ammoniates of [ethylenebis (dithiocarbamate)] zinc with 1 part by weight ethylenebis [dithiocarbamic acid] bimolecular and trimolecular cyclic anhydrosulfides and disulfides, calculated as zinc ethylenebisdithiocarbamate [40 CFR §180.217 and §180.319]. There are currently no tolerances for residues of metiram in any processed food/feed or animal commodities. The Agency has recommended that the tolerance expression for metiram be revised to include residues of ETU.

The current mancozeb and metiram tolerance enforcement method according to PAM, Vol. II is a colorimetric method (designated as Method III), based on the Keppel method (JAOAC, 54:528-532). The Mancozeb and Metiram Reregistration Standard Updates concluded that analytical methods converting EBDCs and some metabolites to carbon disulfide will be considered adequate for enforcement, along with a specific method for ETU. Codex limits for EBDC fungicides are grouped under dithiocarbamates. Limits for the dithiocarbamates are established for 19 commodities resulting from the use of ferbam, ziram, mancozeb, maneb, and zineb (including nabam plus zinc sulfide) and are currently expressed as ppm carbon disulfide. Separate limits (Step 7A) are proposed for ethylene thiourea (ETU) present at harvest on eight commodities (does not include any ETU formed during processing). Harmonization of the U.S. tolerances with Codex MRLs is impractical at the present time.

## CONCLUSIONS AND RECOMMENDATIONS

### Storage Stability Data

1. The submitted storage stability data indicate that fortified residues of mancozeb and metiram are stable at  $-20 \pm 5$  C for ~168 days in apple juice and wet pomace. Residues of ETU are stable for ~60 days in apple juice and wet apple pomace but decline ~27% in both commodities after ~168 days of storage. These storage stability data are adequate to support the submitted apple processing study.

### Magnitude of Mancozeb and Metiram Residue in Apple Processed Commodities

- 2a. The submitted apple processing data indicate that combined residues of mancozeb and ETU will not concentrate in apple juice and wet apple pomace processed from apples treated at 1x maximum the registered use pattern for prebloom treatments or at 1x or 2x the maximum registered use patterns for extended treatments.
- 2b. Five apple processing studies were reviewed in the Residue Chemistry Chapter of the Mancozeb Registration Standard, dated 9/10/86. The average of the concentration/reduction factors determined in those studies, as well as the concentration/reduction factors determined in the current study, is 1.2x for wet pomace. The highest field trial residue (from the previously submitted field trial studies) is <0.501 ppm. Because the expected residues in wet apple pomace (<0.601 ppm) are below the reassessed tolerance for the combined residues of mancozeb and ETU in/on apples (1 ppm), a tolerance for mancozeb residues in wet apple pomace is not required.
- 2c. The submitted apple processing data indicate that combined residues of metiram and ETU will not concentrate in apple juice but may concentrate in wet apple pomace processed from apples treated at 1x maximum the registered use pattern for prebloom treatments or at 1x or 2x the maximum registered use patterns for extended treatments; concentration/reduction factors of 0.8x, 1.0x, and 2.9x were observed for wet pomace.
- 2d. One apple processing study was reviewed in the Residue Chemistry Chapter of the Metiram Registration Standard, dated 9/8/86, and one apple processing study was reviewed in the Metiram Update dated 8/11/92. The average of the concentration/reduction factors determined in those studies, as well as the concentration/reduction factors determined in the current study, is 2.7x for wet pomace. The highest field trial residue (from the previously submitted field trial studies) is 0.5299 ppm. Because the expected residues in wet apple pomace (1.43 ppm) are greater than the reassessed tolerance for the combined residues of metiram and ETU in/on apples (1 ppm), a tolerance for metiram residues in wet apple pomace must be proposed.

- 2c. The following product label amendments are required: (i) the labels for all Rohm and Haas mancozeb products, except EPA Reg. No. 707-235, must be amended to specify that aerial applications are to be made in a minimum of 10 gal/A of water; and (ii) the product label for EPA Reg. No. 7969-70 must be modified to specify that the maximum number of prebloom applications per season is four. In addition, we note that the product label for EPA Reg. No. 707-235 has incorrect calculations of lbs. active ingredient in the "Restrictions" column of the use directions. The first page of the product label states that the product contains 60% by weight of mancozeb; however, all calculations of lbs. active ingredient in the "Restrictions" column seem to be based on the product containing 62.25% ai.

#### Reduction of Residues in/on Apples

- 3a. The submitted mancozeb residue reduction data cannot be used to determine reduction of residues in/on apples during commercial packing as average mancozeb residues were higher in/on apples sampled during the packing procedure than in/on apples sampled prior to packing. Residues of ETU were below the LOQ (<0.005 ppm) in/on all samples; therefore, the extent of reduction of ETU residues during packing cannot be determined.
- 3b. The submitted metiram residue reduction data are adequate to demonstrate reduction of residues in/on apples during commercial packing. Average residues of metiram were 0.417 ppm in/on apples prior to packing, 0.201 ppm (reduction factor of 0.5x) in/on apples sampled after washing in the packing facility, 0.182 ppm (reduction factor of 0.4x) in/on washed apples that had been rinsed by hand to simulate consumer washing, and 0.102 ppm (reduction factor of 0.2x) in/on apples that had been sampled after waxing and then rinsed by hand. These residues reduction data can be used for dietary exposure assessment. Residues of ETU were below the LOQ (<0.005 ppm) in/on all samples; therefore, the extent of reduction of ETU residues during packing cannot be determined.

#### DETAILED CONSIDERATIONS

##### Residue Analytical Methods

Samples of apple commodities from the submitted processing and residue reduction studies were analyzed by Morse Laboratories, Inc. (Sacramento, CA). Mancozeb and metiram residues were determined using GC with flame photometric detection (GC/FPD; Morse Laboratories SOP# Meth-8, Revision #2 or Revision #3), and ETU residues were determined using HPLC with electrochemical detection (HPLC/ECD; Morse Laboratories SOP# Meth-17, Revision #2). Raw data, sample calculations, and representative chromatograms were submitted. Brief discussions of the methods follow.

GC/FPD method: This method converts EBDC residues to carbon disulfide (CS<sub>2</sub>) which is quantitated by GC/FPD. This method is based on methods MTF-88AM-005 and ETU-89AM-001 which have been previously described in conjunction with various field trials. Briefly, residues were extracted with 10% EDTA, 8 N HCl, and 3% stannous chloride solution. The mixture was reacted for 2 hours in a boiling water bath and then maintained at 100 C for analysis. An aliquot of the headspace was analyzed by GC/FPD for CS<sub>2</sub>. The limits of quantitation (LOQs) were 0.01 ppm for whole apples, 0.02 ppm for apple juice and wet apple pomace, and 0.05 ppm for dry apple pomace.

HPLC/ECD method: This method is essentially the same as HPLC method MTF-88-AM-004 which has been previously described in conjunction with various field trials. Briefly, samples were combined with water and the pH was adjusted to 11-12 with ammonium hydroxide. Sodium chloride, Celite, and ethanol were added, and the mixture was filtered through Celite. Water was added and the pH was adjusted (if necessary) to 7-9. The extract was concentrated by rotary evaporation and applied to an alumina column; residues were eluted with ethanol:chloroform (4:96, v:v). The eluate was concentrated and redissolved in water for quantitation by HPLC using a Hypercarb column, an isocratic mobile phase of 1% acetonitrile in 0.02 M phosphoric acid, and electrochemical detection. The LOQs were 0.005 ppm for whole apples and apple juice and 0.01 ppm for wet and dry apple pomace.

Method validation data and concurrent method recovery data from samples separately fortified with mancozeb, metiram, and ETU were provided and are presented in Table 1. For the processing study, apple juice samples used for method validation and concurrent method recovery determinations were purchased commercially. We note that no fortification at the stated LOQ (0.02 ppm) was performed for apple juice for mancozeb or metiram; the registrants stated that low level interferences in the untreated samples prevented fortifications at the LOQ. For the residue reduction study, commercially purchased apples were used for method validation and concurrent method recovery analyses. Apparent residues of mancozeb, metiram, and ETU were below the LOQs (<0.01 ppm for EBDCs and <0.005 ppm ETU) in/on these samples except that detectable residues of mancozeb were observed in/on one whole apple sample at 0.0169 ppm and detectable residues of metiram were observed in/on one whole apple sample at 0.011 ppm (residue reduction study). The recovery data indicate that the GLC/FPD method is adequate for collecting data for residues of mancozeb and metiram, and that the HPLC/ECD method is adequate for collecting data for residues of the metabolite ETU in apples and apple processed commodities.

Table 1. Method validation and concurrent method recoveries of mancozeb, metiram, and ETU from samples of apples separately fortified with mancozeb or metiram at 0.01-1.0 ppm (GLC/FPD) and ETU at 0.005-0.1 ppm (HPLC/ECD).

Matrix	Analyte	Fortification Levels (ppm)	Percent Recovery [mean±standard deviation] <sup>a</sup>	
			Method Validation	Concurrent Method Recovery
Processing Study				
Unwashed apples	Mancozeb	0.01, 0.10	-- <sup>b</sup>	59, 83
	Metiram	0.01, 0.10	--	68, 101
	ETU	0.005, 0.05	--	86, 88
Washed apples	Mancozeb	0.01, 0.10	--	76, 85
	Metiram	0.01, 0.10	--	80, 95
	ETU	0.005, 0.05	--	78, 82
Apple juice	Mancozeb	0.05, 0.50	85-106 (7) [94±11]	72, 88
	Metiram	0.05, 0.50	75-99 (7) [88±11]	92, 108
	ETU	0.005, 0.05	74-84 (7) [80±4]	106, 114
Wet apple pomace	Mancozeb	0.02, 0.20	69; 71-81 (6) [75±5]	73, 86
	Metiram	0.02, 0.20	79-101 (7) [93±7]	87, 102
	ETU	0.01, 0.10	55; 70-76 (6) [70±7]	75, 75
Residue Reduction Study				
Apples	Mancozeb	0.01-0.5	73-88 (5) [82±7.5]	75-98 (3); 145 [101±31]
	Metiram	0.01-1.0	76-110 (6) [93±11]	55; 76-108 (5) [85±20]
	ETU	0.005, 0.05	70-96 (10) [81±9]	90-120 (8) [98±10]

<sup>a</sup> Each recovery value represents one sample unless otherwise indicated in parentheses. Recovery values outside the acceptable 70-120% range are listed separately.

<sup>b</sup> Method validation data for whole apples were reported with the field trial data (CB No. 14373, DP Barcode D207579, 9/6/96, S. Hummel).

### Storage Stability Data

Samples of apple commodities from the submitted processing study were stored at 0-7 C for 39 days and then shipped unfrozen (overnight) to the processing facility, National Food Laboratory (Dublin, CA), where samples were stored at 0 ± 2 C for up to 1 day prior to processing. The processed apple fractions were stored frozen (-24 to -21 C) prior to shipment to the analytical laboratory where samples were stored frozen (-20 ± 5 C) prior to analysis. Treated and untreated samples from the apple processing study were stored 152-164 days (~5 months) from sampling of the processed commodity (including sampling of unwashed apples) to sample analysis.

Samples of apples from the submitted residue reduction study were stored frozen on dry ice after collection and shipped frozen (overnight) to the laboratory where they were stored frozen (-20 ± 5 C) until analysis. Samples were analyzed within 82-104 days (~3 months) of collection.

The registrants conducted a concurrent storage stability study with whole apples in conjunction with the field trial studies; the study indicated that fortified residues of mancozeb and metiram are stable for 7 months and residues of ETU are stable for 3.5 months in/on apples stored frozen at  $-20 \pm 5$  C (CB No. 14373, DP Barcode D207579, 9/6/96, S. Hummel). Residues of ETU in/on whole apples declined ~27% after 7 months (210 days) of storage.

The registrants conducted a concurrent freezer storage stability study on apple juice and wet pomace with the apple processing study. Commercially purchased samples of apple juice and untreated samples of wet apple pomace were used. Samples were fortified separately with mancozeb or metiram at 1.0 ppm, and with ETU at 0.25 ppm and then stored frozen at  $-20 \pm 5$  C. Samples were extracted and analyzed at storage intervals of ~0, 2, 8.5-9, and 24 weeks. Samples were analyzed within 1 day of extraction.

Apparent residues of mancozeb, metiram, and the metabolite ETU in one unfortified sample of each commodity at each storage interval were below the LOQs (<0.02 ppm for mancozeb and metiram in both commodities, <0.005 ppm for ETU in apple juice, and <0.01 ppm for ETU in wet pomace) except that detectable residues of mancozeb were observed in wet pomace at the 9-week storage interval at 0.0927 ppm. The results of the storage stability study are presented in Table 2.

Table 2. Storage stability and concurrent method recoveries of mancozeb, metiram, and ETU, from samples of apple processed commodities fortified separately with mancozeb and metiram at 1.0 ppm and ETU at 0.25 ppm, and stored frozen at  $-20 \pm 5$  C.

Storage Interval (Days)	Storage Stability Recovery (%)			Concurrent Method Recovery (%) <sup>a</sup>		
	Mancozeb	Metiram	ETU	Mancozeb	Metiram	ETU
<b>Apple juice</b>						
0	79, 91	84, 88	89, 96	79, 79 (79)	74, 79 (77)	91, 94 (93)
14	100, 103	91, 91	107, 111	89, 95 (92)	86, 89 (88)	108, 113 (111)
58-59	91, 93	103, 103	83, 90	81, 86 (84)	95, 95 (95)	94, 96 (95)
168	87, 90	117, 124	62, 68	79, 86 (83)	86, 86 (86)	88, 91 (90)
<b>Wet apple pomace</b>						
0	76, 76	83, 83	65, 76	73, 81 (77)	78, 86 (82)	68, 70 (69)
14	81, 81	88, 91	68, 78	77, 81 (79)	88, 91 (90)	79, 79 (79)
61-64	70, 70	83, 83	68, 76	85, 87 (86)	83, 88 (86)	77, 82 (80)
168-172	85, 85	78, 78	64, 65	83, 90 (87)	93, 98 (96)	86, 88 (87)

<sup>a</sup> Average concurrent method recovery in parentheses.

*Study summary:* The submitted storage stability data indicate that fortified residues of mancozeb and metiram are stable at  $-20 \pm 5$  C for ~168 days in apple juice and wet pomace. Residues of ETU are stable for ~60 days in apple juice and wet apple pomace but decline ~27% in both commodities after ~168 days of storage. These storage stability data are adequate to support the submitted apple processing study; the data will be used to correct ETU residues for decline during storage.

### Magnitude of Mancozeb and Metiram Residues in Apple Processed Commodities

*Established tolerances:* A tolerance of 7 ppm has been established for residues of mancozeb in/on apples [40 CFR §180.176]. A tolerance of 2 ppm has been established for residues of metiram in/on apples [40 CFR §180.217]. No mancozeb or metiram tolerances have been established for apple processed food/feed commodities.

*Registered use patterns:* A list of mancozeb products registered to the members of the EBDC/ETU Task Force for use on apples is presented in Table 3. Products are registered for multiple prebloom foliar applications to apples at 4.18-4.8 lb ai/A/application with 7- to 10-day retreatment intervals for a maximum seasonal application rate of 16.7-19.2 lb ai/A, or multiple extended foliar applications to apples at a rate of 2.09-2.4 lb ai A/application with 7- to 10-day retreatment intervals for a maximum seasonal application rate of 14.62-16.8 lb ai/A. Applications may be made using ground or aerial equipment. For Griffin products, applications (both ground and aerial) must be made in a minimum of 50 gal/A. For Rohm and Haas products (except EPA Reg. No. 707-235), aerial applications must be made in a minimum of 2 gal/A; aerial applications in CA must be made in a minimum of 5 gal/A. For Atochem products and Rohm and Haas EPA Reg. No. 707-235, aerial applications must be made in a minimum of 10 gal/A. A PHI of 77 days has been established for extended treatments. Prebloom and extended application schedules are not to be combined. Grazing of livestock in treated orchards is prohibited.

A list of metiram products registered to the members of the EBDC/ETU Task Force for use on apples is presented in Table 3. Products are registered for up to four prebloom foliar applications to apples at a maximum of 4.8 lb ai/A/application with 7- to 10-day retreatment intervals using ground or aerial equipment for a maximum seasonal application rate of 19.2 lb ai/A, or seven extended foliar applications to apples at a maximum rate of 2.4 lb ai A/application with 7- to 10-day retreatment intervals using ground or aerial equipment for a maximum seasonal application rate of 16.8 lb ai/A. Ground applications are to be made in a minimum of 20 gal/A and aerial applications in a minimum of 10 gal/A. A PHI of 77 days has been established for extended treatments. Prebloom and extended application schedules are not to be combined. Grazing of livestock in treated orchards is prohibited.

Table 3. Mancozeb and metiram products registered to the members of the EBDC/ETU Task Force for use on apples.

EPA Reg. No.	Formulation	Label Acceptance Date	Product Name
<b>Rohm and Haas Company</b>			
707-78	80% WP	9/30/98	Dithane —45® Agricultural Fungicide
707-156	4 lb/gal FIC	12/9/99	Dithane F-45® Flowable Mancozeb Agricultural Fungicide
707-162	3.48 lb/gal FIC	10/11/94	Dithane —45® Flowable M Agricultural Fungicide
707-179	70% DF	10/11/94	Dithane® DF/70 Agricultural Fungicide
707-180	75% DF	8/15/97	Dithane DF® Agricultural Fungicide
707-235	60% WP	6/19/97	Maximum® WP Agricultural Fungicide
707-241	80% WP	8/15/97	Dithane® WSP Agricultural Fungicide
<b>Griffin Corporation (mancozeb products transferred from E. I. du Pont de Nemours and Co.)</b>			
1812-360	15% DF	12/19/97	ManKocide® Fungicide/Bactericide
1812-414	75% DF	10/9/98	Manzate® 200 DF Fungicide
1812-415	80% WP	10/28/99	Manzate® 200 Fungicide
1812-416	4 lb/gal FIC	10/9/98	Manzate® 200 Flowable Fungicide
<b>Elf Atochem North America, Inc.</b>			
4581-358	80% WP	8/31/99	Penncozeb® 80WP Fungicide
4581-370	75% DF	8/31/99	Penncozeb® 75DF 75% Dry Flowable Fungicide
<b>Metiram products:</b>			
BASF	7969-70	10/11/94	80% WP
	7969-105	10/11/94	80% DF

The EBDC/ETU Task Force submitted data (1996; MRID 44101101) from apple processing studies. The Task Force had previously submitted data from apple field trials (MRID 43357201; CB No. 14373, DP Barcode D207579, 9/6/96, S. Hummel) conducted using mancozeb and metiram in MI, NY(2), OH, PA, VA, and WA. Apples from one field trial conducted in NY were used in the current processing studies. At one plot of the test site, the mancozeb 75% DF or metiram 80% WP formulation was applied as four prebloom applications to established apple trees at 4.8 lb ai/A/application for a total application rate of 19.2 lb ai/A (1x the maximum seasonal rate for prebloom treatment). At a second plot, the formulation was applied as seven applications at 2.4 lb ai/A/application for a total application rate of 16.8 lb ai/A (1x the maximum seasonal rate for extended treatment). At a third plot, the formulation was applied as seven applications at 4.8 lb ai/A/application for a total application rate of 33.6 lb ai/A (2x the maximum seasonal rate for extended treatment). Applications were made in 55-61 gal/A using tractor-mounted airbase sprayers. Samples were harvested by hand 105 days after the last of four prebloom treatments, or 77 days after the last of seven extended treatments, and were placed in

storage at an apple warehouse at 0-7 C for 39 days and then shipped unfrozen (overnight) to the processing facility, National Food Laboratory (Dublin, CA).

At the processing facility, samples were stored at  $0 \pm 2$  C for up to 1 day prior to processing. Apples were processed according to simulated commercial procedures into clarified juice, wet pomace, and dry pomace. A brief description of the processing procedures follows. Whole apples were washed (5-7 minutes) and quartered, passed through a grinder, and screened into two fractions, unclarified juice and wet pomace. A subsample of the unclarified juice was treated with pectic enzyme at 27-49 C for 1.75 hours, filtered, heated to 88-93 C, and canned as clarified juice.

The processed apple fractions were stored frozen (-24 to -21 C) prior to shipment to the analytical laboratory (Morse Laboratories, Sacramento, CA) where samples were stored frozen ( $-20 \pm 5$  C) prior to analysis. Residues of mancozeb or metiram, and ETU were determined using the GLC/FPD and HPLC/ECD methods described in the "Residue Analytical Method" section. We note that the submission contained data for dry apple pomace; these data are not presented here as the Agency no longer considers dry apple pomace to be a significant livestock feed item.

The results of the processing study are presented in Table 4. Apparent residues of mancozeb and ETU were nondetectable ( $<0.01$  ppm and  $<0.005$  ppm, respectively) in/on one sample each of unwashed and washed apples and were nondetectable ( $<0.02$  and  $<0.01$  ppm, respectively) in one sample of wet pomace from the mancozeb trial. Apparent residues of metiram and ETU were nondetectable ( $<0.01$  ppm and  $<0.005$  ppm, respectively) in one sample each of unwashed and washed apples and were nondetectable ( $<0.02$  and  $<0.01$  ppm, respectively) in one sample of wet pomace from the metiram trial. Detectable residues of mancozeb (0.1771 ppm) and metiram (0.0557 ppm) were found in one sample of untreated apple juice each from the mancozeb and metiram trial. We note that untreated juice samples were obtained commercially. The registrants concluded that detectable residues in untreated juice may have resulted from contamination in the laboratory.

The concurrent storage stability data submitted with this study (see "Storage Stability Data") indicated that residues of ETU would decline ~27% in whole apples, apple juice, and wet apple pomace during 168 (apple juice and pomace) or 210 days (whole apples) of storage. ETU residues were below the LOQ in/on all commodities. If the LOQ for each commodity is corrected for a possible 30% decline during storage, the LOQs for ETU in apple commodities become 0.007 ppm (whole apples and apple juice) and 0.013 ppm (wet apple pomace). Because EBDC residues were generally quantifiable and much greater than the ETU LOQs, correcting the ETU LOQs for decline during storage would not have a significant effect on combined residues levels or concentration/reduction factors. Therefore, no corrections have been made to the data in Table 4.

Table 4. Residues of mancozeb, metiram, and ETU in commodities processed from apples harvested either 105 days following the last of four prebloom applications of the mancozeb 75% DF formulation or metiram 80% WP formulation at 4.8 lb ai/A/application (1x the maximum seasonal rate for prebloom treatment), or 77 days following the last of seven extended applications of the mancozeb 75% DF formulation or metiram 80% WP formulation at 2.4 or 4.8 lb ai/A/application (1x or 2x the maximum seasonal rate for extended treatment, respectively).

Apple Commodity	Residues, ppm <sup>a</sup>			Concentration/Reduction Factor <sup>b</sup>		
	EBDC	ETU	Combined	EBDC	ETU	Combined
<b>Mancozeb - Four applications at 4.8 lb ai/A/application (1x - prebloom)</b>						
Unwashed	0.0911	<0.005	<0.0961	--	--	--
Washed	0.0365	<0.005	<0.0415	0.4x	--	0.4x
Juice	<0.02	<0.005	<0.025	<0.2x	--	0.3x
Wet pomace	0.0700	<0.01	<0.0800	0.8x	--	0.8x
<b>Mancozeb - Seven applications at 2.4 lb ai/A/application (1x - extended)</b>						
Unwashed	0.1012	<0.005	<0.1062	--	--	--
Washed	0.0702	<0.005	<0.0752	0.7x	--	0.7x
Juice	<0.02	<0.005	<0.025	<0.2x	--	0.2x
Wet pomace	0.0777	<0.01	<0.0877	0.8x	--	0.8x
<b>Mancozeb - Seven applications at 4.8 lb ai/A/application (2x - extended)</b>						
Unwashed	0.2174	<0.005	<0.2224	--	--	--
Washed	0.2331	<0.005	<0.2381	1.1x	--	1.1x
Juice	<0.02	<0.005	<0.025	<0.1x	--	0.1x
Wet pomace	0.2140	<0.01	<0.2240	1.0x	--	1.0x
<b>Metiram - Four applications at 4.8 lb ai/A/application (1x - prebloom)</b>						
Unwashed	0.0513	<0.005	<0.0563	--	--	--
Washed	0.0634	<0.005	<0.0684	1.2x	--	1.2x
Juice	<0.02	<0.005	<0.025	<0.4x	--	0.4x
Wet pomace	0.1520	<0.01	<0.1620	3.0x	--	2.9x
<b>Metiram - Seven applications at 2.4 lb ai/A/application (1x - extended)</b>						
Unwashed	0.1858	<0.005	<0.1908	--	--	--
Washed	0.1486	<0.005	<0.1536	0.8x	--	0.8x
Juice	<0.02	<0.005	<0.025	<0.1x	--	0.1x
Wet pomace	0.1406	<0.01	<0.1506	0.8x	--	0.8x
<b>Metiram - Seven applications at 4.8 lb ai/A/application (2x - extended)</b>						
Unwashed	0.3019	<0.005	<0.3069	--	--	--
Washed	0.1926	<0.005	<0.1976	0.6x	--	0.6x
Juice	<0.02	<0.005	<0.025	<0.1x	--	0.1x
Wet pomace	0.2951	<0.01	<0.3051	1.0x	--	1.0x

<sup>a</sup> Residues were not corrected for concurrent method recovery.

- <sup>b</sup> Concentration/reduction factors were calculated relative to unwashed apples, but could not be calculated for ETU because all values were less than the LOQ.

*Study summary:* The submitted apple processing data indicate that combined residues of mancozeb and ETU will not concentrate in apple juice and wet apple pomace processed from apples treated at 1x maximum the registered use pattern for prebloom treatments or at 1x or 2x the maximum registered use patterns for extended treatments.

Five apple processing studies were reviewed in the Residue Chemistry Chapter of the Mancozeb Registration Standard, dated 9/10/86. The results of these studies are presented in Table 5. The average of these concentration/reduction factors, as well as the concentration/reduction factors determined in the current study, is 1.2x for wet pomace. The highest field trial residue (from the previously submitted field trial studies) is <0.501 ppm. Because the expected residues in wet apple pomace (<0.601 ppm) are below the reassessed tolerance for the combined residues of mancozeb and ETU in/on apples (1 ppm), a tolerance for mancozeb residues in wet apple pomace is not required.

The submitted apple processing data indicate that combined residues of metiram and ETU will not concentrate in apple juice but may concentrate in wet apple pomace processed from apples treated at 1x maximum the registered use pattern for prebloom treatments or at 1x or 2x the maximum registered use patterns for extended treatments; concentration/reduction factors of 0.8x, 1.0x, and 2.9x were observed for wet pomace.

One apple processing study was reviewed in the Residue Chemistry Chapter of the Metiram Registration Standard, dated 9/8/86, and one apple processing study was reviewed in the Metiram Update dated 8/11/92; the results of these studies are presented in Table 5. The average of these concentration/reduction factors, as well as the concentration/reduction factors determined in the current study, is 2.7x for wet pomace. The highest field trial residue (from the previously submitted field trial studies) is 0.5299 ppm. Because the expected residues in wet apple pomace (1.43 ppm) are greater than the reassessed tolerance for the combined residues of metiram and ETU in/on apples (1 ppm), a tolerance for metiram residues in wet apple pomace must be proposed.

The following product label amendments are required: (i) the labels for all Rohm and Haas mancozeb products, except EPA Reg. No. 707-235, must be amended to specify that aerial applications are to be made in a minimum of 10 gal/A of water; and (ii) the product label for EPA Reg. No. 7969-70 must be modified to specify that the maximum number of prebloom applications per season is four. In addition, we note that the product label for EPA Reg. No. 707-235 has incorrect calculations of lbs. active ingredient in the "Restrictions" column of the use directions. The first page of the product label states that the product contains 60% by weight of mancozeb; however, all calculations of lbs. active ingredient in the "Restrictions" column seem to be based on the product containing 62.25% ai.

Table 5. Previously reported residues of mancozeb, metiram, and ETU in unwashed apples and wet apple pomace from apple processing studies reviewed in the Mancozeb Registration Standard, dated 9/10/86, the Metiram Registration Standard, dated 9/8/86, and the Metiram Update, dated 8/11/92.

Apple Commodity	Residues, ppm			Concentration/Reduction Factor <sup>a</sup>		
	EBDC	ETU	Combined	EBDC	ETU	Combined
<b>Mancozeb - Registration Standard - MI-1</b>						
Unwashed	1.5-1.9	<0.01	<1.51-<1.91	--	--	--
Wet pomace	1.7	<0.01-0.033	<1.71-1.733	1.0x	>3.3x	1.0x
<b>Mancozeb - Registration Standard - MI-2</b>						
Unwashed	7.0	0.011	7.011	--	--	--
Wet pomace	4.0	0.059	4.059	0.6x	5.4x	0.6x
<b>Mancozeb - Registration Standard - OH</b>						
Unwashed	8.8	0.01-0.015	8.81-8.815	--	--	--
Wet pomace	1.9	0.039	1.939	0.2x	3.1x	0.2x
<b>Mancozeb - Registration Standard - PA-1</b>						
Unwashed	4.4, 4.6	<0.03	<4.43, <4.63	--	--	--
Wet pomace	13, 14.1	<0.03	<13.03, <14.13	3.0x	--	3.0x
<b>Mancozeb - Registration Standard - PA-2</b>						
Unwashed	6.2, 7.4	<0.03	<6.23, <7.43	--	--	--
Wet pomace	17, 17.6	<0.03	<17.03, <17.63	2.5x	--	2.5x
<b>Metiram - Registration Standard</b>						
Unwashed	3.6, 3.9	0.03, 0.04	3.63, 3.94	--	--	--
Wet pomace	16	0.08	16.08	4.3x	2.3x	4.2x
<b>Metiram - Update</b>						
Unwashed	2.2	0.07	2.27	--	--	--
Wet pomace	10.2	0.22	10.42	4.6x	3.1x	4.6x

<sup>a</sup> Concentration/reduction factors were calculated using average residues when more than one residue value was reported. When a range of residue values was reported, the average was calculated as the mean of the lowest and highest residue.

### Reduction of Residues in/on Apples

The EBDC/ETU Task Force submitted data (1996; MRID 44064001) pertaining to the reduction of residues of mancozeb, metiram, and ETU in/on apples resulting from commercial packing and consumer washing. Two packing houses (in NY and PA) were selected based on the availability of apples treated with mancozeb or metiram at rates close to the maximum registered rates. At the NY site, golden delicious apples were harvested 90-103 days following the last of nine applications of the 75% DF mancozeb formulation (EPA Reg. No. 4581-370) at 1.25-2.25 lb

ai/A/application for a total seasonal rate of 13.5 lb ai/A (0.8x the maximum rate for extended treatment). Apples samples were stored at ~0 C for 17-22 days prior to the initiation of the packing process. At the PA site, red delicious apples were harvested 108-113 days following the last of nine applications of the 80% WP metiram formulation (EPA Reg. No. 7969-70) at 1.2 lb ai/A/application for a total seasonal rate of 10.8 lb ai/A (0.6x the maximum rate for extended treatment). Apples were stored at ~0 C for 22-24 days prior to the initiation of the packing process.

A brief description of the packing process follows. The apples were first washed in a water tank for approximately 5-10 minutes and then are transferred to a conveyor belt where they were sprayed with water; at the PA packing house the apples were sprayed with detergent before the water rinse. Following the water rinse the apples passed through a chain eliminator system which removed the smallest apples. The apples were then brushed with cloth brushes and exposed to heated air to dry. The apples then passed under a wax sprayer and were dried under fans with heated air; the apples were tumbled as they were dried to polish them. The apples were inspected and damaged apples were removed by hand. The apples were then sorted mechanically and distributed for hand packing into bags or cardboard boxes. The apples were returned to storage at ~0 C until shipping.

For this study, samples of apples were collected from storage prior to packing, after the washing procedure, and after the waxing procedure. In addition, some of the apples collected after the washing procedure and after the waxing procedure were rinsed by hand with rubbing under a stream of water to simulate consumer washing. The apples were frozen on dry ice after collection and shipped frozen to the laboratory (Morse Laboratories, Sacramento, CA), where samples were stored frozen ( $-20 \pm 5$  C) prior to analysis. Residues of mancozeb or metiram, and ETU were determined using the GLC/FPD and HPLC/ECD methods described in the "Residue Analytical Method" section.

The results of the residue reduction study are presented in Table 6.

Table 6. Residues of mancozeb, metiram, and ETU in apple commodities sampled prior to and during packing at commercial packing houses.

Apple Commodity	Residues, ppm <sup>a</sup>		Concentration/Reduction Factor <sup>b</sup>	
	EBDC	ETU	EBDC	ETU
<b>Mancozeb - Total seasonal application rate of 13.5 lb ai/A</b>				
Unwashed	0.030-0.048 [0.038±0.008]	<0.005	--	--
Washed	0.055-0.186 [0.105±0.061]	<0.005	2.8x	--
Consumer washed <sup>c</sup>	0.034-0.115 [0.060±0.038]	<0.005	1.6x	--
Waxed and consumer washed <sup>d</sup>	0.045-0.076 [0.060±0.013]	<0.005	1.6x	--
<b>Metiram - Total seasonal application rate of 10.8 lb ai/A</b>				
Unwashed	0.304-0.731 [0.417±0.210]	<0.005	--	--
Washed	0.118-0.262 [0.201±0.069]	<0.005	0.5x	--
Consumer washed	0.099-0.245 [0.182±0.070]	<0.005	0.4x	--
Waxed and consumer washed	0.076-0.162 [0.102±0.041]	<0.005	0.2x	--

<sup>a</sup> Residues were not corrected for concurrent method recovery. The reported residues represent four samples of each commodity. The mean and standard deviation of the residues is presented in brackets.

<sup>b</sup> Concentration/reduction factors were calculated from the average residue relative to the average residue for unwashed apples.

<sup>c</sup> Apples sampled after the washing procedure and then rinsed by hand with rubbing under a stream of water to simulate consumer washing.

<sup>d</sup> Apples sampled after the waxing procedure and then rinsed by hand with rubbing under a stream of water to simulate consumer washing.

*Study summary:* The submitted mancozeb residue reduction data cannot be used to determine reduction of residues in/on apples during commercial packing as average mancozeb residues were higher in/on apples sampled during the packing procedure than in/on apples sampled prior to packing. Residues of ETU were below the LOQ (<0.005 ppm) in/on all samples; therefore, the extent of reduction of ETU residues during packing cannot be determined.

The submitted metiram residue reduction data are adequate to demonstrate reduction of residues in/on apples during commercial packing. Average residues of metiram were 0.417 ppm in/on apples prior to packing, 0.201 ppm (reduction factor of 0.5x) in/on apples sampled after washing in the packing facility, 0.182 ppm (reduction factor of 0.4x) in/on washed apples that had been rinsed by hand to simulate consumer washing, and 0.102 ppm (reduction factor of 0.2x) in/on

apples that had been sampled after waxing and then rinsed by hand. These residues reduction data can be used for dietary exposure assessment. Residues of ETU were below the LOQ (<0.005 ppm) in/on all samples; therefore, the extent of reduction of ETU residues during packing cannot be determined.

#### EPA MEMORANDA CITED IN THIS REVIEW

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#### MASTER RECORD IDENTIFICATION NUMBERS

Citations for the MRID documents referred to in this review are presented below.

44064001 Bennett, R.; Honeycutt, R. (1996) EBDC Residues—Commercial Apple Preparation: Lab Project Number: 94-403RA: ETU-94-APP: 95-514. Unpublished study prepared by Morse Labs., Inc. 496 p.

44101101 Bennett, R.; Honeycutt, R. (1996) 1992 Mancozeb and Metiram Apple Processing Study: Final Report: Lab Project Number: 92-203RA-P: ETU-92-APP-92-203RA-P: ETU-92-APP-P: 95-515. Unpublished study prepared by Morse Laboratories, Inc. and The National Food Laboratory. 1328 p.